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(54) **PROCESS FOR REMOVING ARSENIC FROM PETROLEUM FRACTION.**

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Description

Technical Field

5 This invention relates to a process for removing arsenic from a petroleum fraction and, more particularly, to a process for efficiently removing arsenic from particularly a light petroleum fraction such as naphtha.

If arsenic (As) is contained in petroleum fractions such as straight run naphtha, kerosene and fractions formed by catalytic cracking or the like, then in producing petrochemical starting materials such as ethylene or petrochemical products such as polymers from the petroleum fraction using a catalyst, poisoning of the catalyst
10 by arsenic will occur and the catalytic activity will be rapidly reduced or coking will be accelerated in the pyrolysis of the petroleum fractions. Particularly, when noble metals such as Pt and Pd are used as catalysts, the catalysts can be significantly and adversely affected even if arsenic is present in a minor amount. It is highly desired that arsenic is removed from petroleum fractions such as straight run naphtha to a specific amount or below.

Various processes for removing arsenic from a petroleum fraction have been known in the prior art. Such
15 processes include a process wherein a petroleum fraction is subjected to hydrodesulfurization treatment to remove arsenic together with sulfur. According to this process, arsenic is removed together with sulfur. However, when the removal of arsenic is desired, the installation cost and running cost are increased. Further, the process is unsuitable for feed naphtha having a small arsenic content for a steam cracker. There has been proposed another process wherein a petroleum fraction is brought into contact with an alkali metal or alkaline earth
20 metal, and a further process wherein a petroleum fraction is brought into contact with either a nitrogen-containing compound having three substituted moieties and one unpaired electron or a lignite active carbon. However, these processes have such problems that the dearsination ability is low and a large amount of a dearsinating agent is required.

Further, there has been proposed a process wherein arsenic contained in a petroleum fraction is directly
25 oxidized with an oxidizing agent such as an organic peroxide to form heavy products and such heavy products are distilled and separated. However, when highly reactive olefins are contained in the petroleum fraction, these olefins may be polymerized or oxidized to cause the generation of troubles.

There has been known a further process wherein arsenic contained in a petroleum fraction is brought into contact with a copper impregnated active carbon to remove arsenic. However, this process has such problems
30 that this copper impregnated active carbon is expensive and the percent removal of arsenic is not always satisfactory.

We have carried out studies in order to overcome such problems and to efficiently remove arsenic from a petroleum fraction. We have now found that, when the petroleum fraction is brought into contact with a specific adsorbent, arsenic can be efficiently removed. The present invention has been completed on the basis of such
35 a discovery.

The present invention is intended to overcome the problems associated with the prior art as described above. An object of the present invention is to provide a process for removing arsenic from a petroleum fraction, wherein arsenic which is a poison for the catalyst can be easily and efficiently removed from the petroleum fraction and wherein, even if highly reactive olefins are contained in the petroleum fraction, these olefins are
40 not polymerized in the course of the removal of arsenic, thus no troubles occur.

The process for removing arsenic in a petroleum fraction according to the present invention comprises contacting the petroleum fraction containing arsenic with an adsorbent, said adsorbent comprising a substrate such as an active carbon, bituminous coal or organic polymeric compound having introduced therein a sulfur-containing component selected from mercapto moieties, thioethers, thioaldehydes, thiocarboxylic acids, dithiocarboxylic acid, thioamides and thiocyanates.
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Accordingly, arsenic in the petroleum fraction can be removed at a high percent removal by means of simple equipment, and, even if highly reactive olefins are contained in the petroleum fraction, these olefins are not polymerized, thereby troubles can be avoided.

While it has been heretofore known that polymeric compounds having an aromatic moiety or compounds
50 obtained by introducing a mercapto moiety into a vinyl chloride resin adsorb heavy metals such as mercury, cadmium, chromium, lead and arsenic contained in wastewater, it has been not known at all that the adsorbent specified by the present invention can easily remove arsenic in the petroleum fraction at a high percent removal without any troubles, i.e., without polymerizing highly reactive olefins even if these olefins are contained in the petroleum fraction.

55 A process for removing arsenic in a petroleum fraction according to the present invention will be fully described hereinafter.

Petroleum fractions from which arsenic is to be removed in the present invention include fractions such as straight run naphtha (directly distilled off from crude oils), kerosene, gas oil and vacuum gas oil; light fractions

formed by heat treatment in ethylene plants, cokers, visbreakers or the like; and light fractions formed by fluid catalytic cracking treatment. Further, in the present invention, relatively light fractions such as condensate (NGL) can be used as the petroleum fractions.

Arsenic is usually contained in such petroleum fractions in the form of hydrides or organic compounds as represented by the formula R_nAsH_{3-n} wherein R is an alkyl or phenyl moiety etc. and n is 0,1,2 or 3.

Examples of such arsenic compounds include arsine monomethylarsine, dimethylarsine, trimethylarsine, tributylarsine, and triphenylarsine. Arsenic can also be contained in the petroleum fractions in the form of halogenated arsenic compounds such as dimethylchloroarsine or oxidized arsenic compounds such as trimethylarsine oxide.

While the kind of arsenic compound can be varied depending upon the type of the petroleum fractions arsenic is generally contained in the petroleum fractions at a level of from several ppb (by weight) to hundreds of ppb (by weight) in many cases.

In order to accurately analyze the amount of arsenic contained in such petroleum fractions, for example the following method found by us can be utilized.

That is, it is possible to utilize a method wherein an oxidizing agent and an acid are added to a petroleum fraction containing an organoarsenic compound to convert said organoarsenic compound to an arsenic oxide; the resulting arsenic oxide is then reduced to form an arsenic hydride; this arsenic hydride is heated to form atomic arsenic; and the amount of atomic arsenic is determined by an atomic absorption method.

In the method, the organoarsenic compound contained in the petroleum fraction is oxidized to form the arsenic oxide, the arsenic oxide is then reduced to form the arsenic hydride and thereafter the quantitative analysis is carried out by the atomic absorption method. Accordingly, the quantitative analysis of arsenic can be carried out within an extremely short period of time with good precision and reproducibility. Further, an oxyhydrogen flame or the like is not used and therefore the safety is extremely high. Furthermore, an extremely minor amount of arsenic can also be analyzed.

The method of analyzing arsenic in the petroleum fraction as described above will be fully described.

An organoarsenic compound contained in a petroleum fraction is relatively high in its vapor pressure and liable to be volatilized by heating. Accordingly, it is necessary to carry out pretreatment before analysis of arsenic.

First, an oxidizing agent and an acid are added to the petroleum fraction containing the organoarsenic compound to oxidize and decompose the organoarsenic compound to form an arsenic oxide, and this arsenic oxide is extracted in an aqueous phase.

Such oxidizing agents for use herein include hydrogen peroxide, potassium bichromate, potassium oxalate, potassium permanganate, nitric acid and organic peroxides.

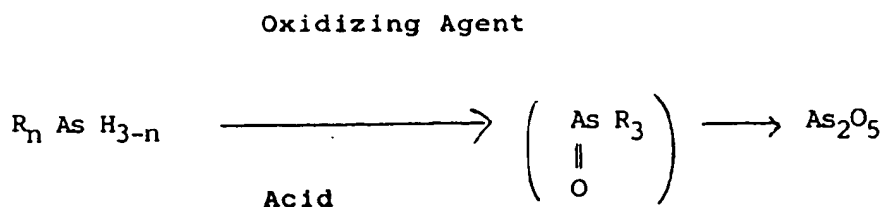
When aqueous hydrogen peroxide is used as the oxidizing agent, it is desirable that its concentration is of the order of from 10% to 30% by weight.

The acids for use herein include sulfuric acid, hydrochloric acid and nitric acid.

It is preferable that the acid added has a high concentration, i.e., at least 50% by weight.

In oxidizing and decomposing the organoarsenic compound contained in the petroleum fraction to form the arsenic oxide, the above oxidizing agent such as aqueous hydrogen peroxide is preferably first added to the petroleum fraction, and then to the resulting mixture is added a mixture of the oxidizing agent and the acid, e.g., a mixture of aqueous hydrogen peroxide and sulfuric acid. Alternatively, a mixture of an oxidizing agent and an acid can also be directly added to the petroleum fraction.

As the organoarsenic compound in the petroleum fraction is thus oxidized and decomposed, the organoarsenic compound will be converted to an arsenic oxide as shown in the following formula:



While the amount of a petroleum fraction sample used in carrying out the quantitative analysis of arsenic can be largely varied depending upon the content of arsenic, it is generally of the order of from 5 to 100ml. For example, when 500wt ppb of arsenic is contained in the petroleum fraction, 5ml of the sample is sufficient. When the content of arsenic is 100wt ppb, from 20 to 25ml of the sample is used. When the content of arsenic is from

20 to 50wt ppb, from 30 to 50ml of the sample is used. When the content of arsenic is from 2 to 10wt ppb, about 100ml of the sample is used.

It is preferable to heat the reaction system to a refluxing temperature during the oxidation/decomposition of the organoarsenic compound contained in the petroleum fraction as described above or after oxidation/decomposition. By thus heating, hydrocarbons in the sample are decomposed or evaporated and removed, and the resulting arsenic oxide is transferred to an aqueous phase. During this time, even if excess oxidizing agents such as hydrogen peroxide are present in the reaction system, they are decomposed. If the oxidizing agents such as hydrogen peroxide remain in the aqueous phase in the atomic absorption analysis described hereinafter, the quantitative analysis of arsenic is adversely affected. Therefore, the residual oxidizing agents are undesirable for the atomic absorption analysis.

In some cases, a portion of the petroleum fraction is carbonized during the heating step. In the case of such petroleum fractions, a large amount of the oxidizing agent such as hydrogen peroxide can be used to decompose the carbonized petroleum fraction, thereby removing it.

The arsenic oxide obtained by oxidizing as described above is then reduced to form an arsenic hydride. It is believed that the reduction of the arsenic oxide to the arsenic hydride proceeds as shown in the following formula:



The reduction of the arsenic oxide to the arsenic hydride is preferably carried out by adding sodium boron hydride to the reaction system. The sodium boron hydride is also preferably added to the reaction system in the form of an aqueous solution. During this time, acids such as hydrochloric acid are preferably added to the aqueous solution to acidify it. It is also preferable that the concentration of the aqueous sodium boron hydride solution is of the order of from 1% to 5% by weight. Further, sodium boron hydride is used in an excess amount relative to the arsenic oxide to be reduced.

In the reduction of the arsenic oxide by sodium boron hydride as described above, the coexistence of potassium iodide in the reaction system promotes the reduction of arsenic (v) oxide to arsenic (III) oxide, and the sensitivity of the analysis of arsenic is improved. The potassium iodide is present in the reaction system at a level of from 0.1% to 10% by weight, preferably from 0.5% to 5% by weight.

After the organoarsenic compound in the petroleum fraction is thus converted to the arsenic hydride (AsH_3), this arsenic hydride is heated to form atomic arsenic and this atomic arsenic is subjected to quantitative analysis by an atomic absorption analysis method.

In heating the arsenic hydride to form the atomic arsenic, the arsenic hydride is heated to a conventional temperature used in the prior art heating/atomization method of the arsenic hydride, e.g., to a temperature of the order of from about 800°C to 1,100°C by means of commercially available hydride atomization apparatus. The quantitative analysis of the resulting atomic arsenic can be carried out by means of commercially available atomic absorption apparatus. The conditions or the like used in such steps can be conventional conditions utilized in the prior art atomic absorption analysis of arsenic.

In the present invention, the petroleum fraction having arsenic is brought into contact with an adsorbent comprising a substrate such as an active carbon, bituminous coal or organic polymeric compound having introduced therein a sulfur-containing component.

The active carbon used as the substrate is in the form of powder or granules. It is desirable that its specific surface area is from 200 to 2,000 square meter per gram, preferably from 500 to 1,500 square meter per gram.

The bituminous coal is used in the form of powder or granules as with the active carbon.

The organic polymeric compounds used as the substrate maybe polystyrene, styrene-divinylbenzene copolymers, polyvinyl chloride, phenolic resins, cellulose or mixtures thereof.

Of the above, the particularly preferred substrate is active carbon.

The sulfur-containing component introduced into these substrates is either a mercapto moiety, or may be selected from thioethers, thioaldehydes, thiocarboxylic acids, dithiocarboxylic acids, thioamides and thiocyanates.

In order to introduce the sulfur-containing component into the substrate in the form of a mercapto moiety, for example, a process as described in Japanese Patent Publication No.45924/1981 can be utilized. That is, the substrate may be chloromethylated and thereafter reacted with an alcoholic alkali hydrosulfide. Alternatively, the substrate may be chlorosulfonated and thereafter the introduced chlorosulfone moiety may be reduced. Further, in the case of a cellulose substrate, a method as described in Japanese Patent Publication No.15554/1977 can also be utilized.

It is believed that, when the adsorbent comprising the substrate having the sulfur element introduced therein is used for removing arsenic, the reason why the removal efficiency of arsenic is improved as compared with the adsorbent having no sulfur element introduced resides in the fact that sulfur in the adsorbent acts as a donor. It is also believed that, particularly when active carbon is used as the substrate the adsorption reaction

by the active carbon occurs and therefore the removal efficiency of arsenic is enhanced.

Contact Condition

5 The contact of the petroleum fraction containing arsenic with the adsorbent can be carried out by optional methods known in the prior art. For example, it is possible to utilize a method wherein the petroleum fraction containing arsenic is brought into contact with the adsorbent in a liquid phase state in a fixed bed system; another method wherein the petroleum fraction containing arsenic is brought into contact with the adsorbent in a liquid phase state in a moving bed system; and a further method wherein the petroleum fraction containing
10 arsenic is brought into contact with the adsorbent in a liquid phase state in a fluidized bed system. Further optionally, the petroleum fraction can be brought into contact with the adsorbent in a batch system.

The contact of the petroleum fraction with the adsorbent is carried out at a liquid hourly space velocity (L. H. S. V.) of the order of from 0.01 to 20hr⁻¹, preferably from 1 to 10hr⁻¹. The temperature during the contact is of the order of from 0°C to 100°C.

15 In the present invention, the petroleum fraction containing arsenic is brought into contact with the adsorbent comprising the substrate such as active carbon, bituminous coal or organic polymeric compound having introduced therein the sulfur element, for example in the form of a mercapto moiety. Accordingly, arsenic in the petroleum fraction can be removed at a high percent removal by means of a simple equipment.

That is, in order to remove arsenic from the petroleum fraction containing arsenic by the present invention, pretreatment installation and posttreatment installation other than strainers are unnecessary. Moreover, even
20 if highly reactive olefins are contained in the petroleum fraction, these olefins will not be polymerized and thus no troubles will occur.

While the present invention is illustrated by Examples, it is not limited thereto.

25 Example 1

First, according to the process described in Japanese Patent Laid-open Publication No.117585/1974, mercapto moieties were introduced into a coconut husk active carbon as described hereinafter. That is, 90ml of chloromethyl ether and 30 grams of tetrachloroethane were added to 30 grams of the coconut husk active carbon, and the resulting mixture was allowed to stand for 30 minutes at room temperature. Thirty grams of aluminum chloride anhydride were then gradually added at a temperature of from 0°C to 5°C over about two hours to carry out the chloromethylation of the active carbon. After the reaction, water was gradually added into the resulting mixture kept in an ice bath to hydrolyze the unreacted material. The resulting chloromethylated active carbon was separated from the aqueous phase, sequentially thoroughly washed with water and acetone, and
35 thereafter dried.

To 30 grams of the resulting dried chloromethylated active carbon were added 100ml of ethanol and 200ml of a 20% aqueous potassium hydrosulfide solution, and the reaction mixture was reacted for 3 hours at room temperature. The resulting mercapto moietycontaining compound was repeatedly washed with 1 mole/liter of ammonium hydroxide until the basicity was substantially disappeared. The resulting active carbon having mercapto moieties contained 0.19% by weight of sulfur.
40

A column having a diameter of 8mm and a length of 100mm was packed with 5ml of the thus obtained active carbon having mercapto moieties. Light naphtha containing 36ppb (by weight) of arsenic was passed through the column at a liquid hourly space velocity (L.H.S.V.) of 10hr⁻¹.

When the total throughput was 4,000 liters per liter of the adsorbent, the thus treated light naphtha contained 5ppb (by weight) of arsenic. The percent removal of arsenic was 86%.
45

Comparative Example 1

The arsenic removal procedure was carried out as in Example 1 except that a coconut husk active carbon having no mercapto moieties introduced therein was used as an adsorbent.
50

When the total throughput was 4,000 liters per liter of adsorbent, the thus treated light naphtha contained 12ppb (by weight) of arsenic, and the percent removal of arsenic was 67%.

Example 2

55 In Example 1, the coconut husk active carbon was replaced with a high porous polymer (polystyrene type polymer available from Mitubishi Kasei, K.K. under the tradename Dia Ion HP-10), and mercapto moieties were introduced into this polymer as in Example 1. Arsenic in light naphtha containing 36ppb of arsenic was removed

as in Example 1 using the resulting high porous polymer having mercapto moieties introduced therein.
Until the total throughput reached 3,000 liters per liter of adsorbent, 80% of arsenic was removed.

Comparative Example 2

40ml of a high porous polymer having no mercapto moieties introduced therein was contacted and mixed with 400ml of a light naphtha containing 440ppb of arsenic for one hour to remove arsenic in the light naphtha.
The thus treated light naphtha contained 420ppb of arsenic, and the percent removal of arsenic was 4.5%.

Comparative Example 3

A coconut husk active carbon having no mercapto moieties introduced therein was impregnated with copper to prepare a copper impregnated active carbon which has been heretofore used in removing arsenic from petroleum fractions.

40ml of this copper impregnated active carbon was contacted and mixed with 400ml of a light naphtha containing 410ppb of arsenic for one hour to remove arsenic in the light naphtha.

The thus treated light naphtha contained 170ppb of arsenic, and the percent removal of arsenic was 61%.

Example 3

The adsorbent produced in Example 1 was used, and 1,000ppb (by weight) of tributylarsine was added to a China naphtha containing 220ppb (by weight) of arsenic. A test for adsorbing arsenic was carried out at an L. H. S. V. of 5 hr⁻¹ and at room temperature. The results are shown in Table 1.

TABLE 1

| Feed Naphtha | Total Throughput (liter of naphtha/ liter of adsorbent) | Percent Removal of Arsenic(%) |
|-------------------------|---|-------------------------------------|
| Tributylarsine added | 700 | >99 |

Example 4

A test was carried out under the same conditions as those described in Example 3 except that the adsorbent produced in Example 2 was used. The results are shown in Table 2.

TABLE 2

| Feed Naphtha | Total Throughput (liter of naphtha/ liter of adsorbent) | Percent Removal of Arsenic(%) |
|---------------------------------|--|--|
| Tributylarsine added | 700 | >99 |

The following Reference Examples describe an analysis of arsenic in a petroleum fraction.

Reference Example 1

20ppb (by weight) of triphenylarsine was added as an organoarsenic compound to 100ml of a light naphtha which was substantially free of an organoarsenic compound. To this light naphtha were added 20ml of 31% aqueous hydrogen peroxide and 30ml of 18N sulfuric acid to oxidize and decompose arsenic to form an arsenic oxide and to remove hydrocarbons in the naphtha. Further, this reaction mixture was heated for about 10 minutes at a refluxing temperature of water to decompose the residual excess hydrogen peroxide.

To the thus obtained aqueous solution containing the arsenic oxide was added 5ml of a 40% by weight aqueous potassium iodide solution, and the resulting mixture was allowed to stand for about 30 minutes. Thereafter, this aqueous solution and the same volume of a 2% by weight aqueous sodium boron hydride solution were individually introduced into each hydride generation apparatus (HYD-1 manufactured by Nippon Jourrel Ash) to reduce the arsenic oxide to arsenic hydride (AsH_3).

The thus obtained arsenic hydride AsH_3 was introduced into a commercially available hydride atomization apparatus (HYD-2 manufactured by Nippon Jourrel Ash), and arsenic hydride was decomposed at an atomizer temperature of 1,000°C to form atomic arsenic. The thus obtained atomic arsenic was introduced into a commercially available atomic absorption apparatus (AA-8200 manufactured by Nippon Jourrel Ash), and arsenic was determined from the absorbance of an atomic absorption photometer at 193.7mm.

The quantitative analysis procedure of arsenic as described above was completed for about 2 hours.

This procedure was repeated 20 times to examine the analysis precision and reproducibility.

The results are shown in Table 3.

TABLE 3

| No. | Analyzed Arsenic Concentration (wt ppb) | No. | Analyzed Arsenic Concentration (wt ppb) |
|-----|--|-----|--|
| 1 | 19.5 | 11 | 20.5 |
| 2 | 21.5 | 12 | 21.5 |
| 3 | 20.5 | 13 | 19.0 |
| 4 | 21.5 | 14 | 21.5 |
| 5 | 19.5 | 15 | 19.5 |
| 6 | 21.5 | 16 | 21.5 |
| 7 | 20.0 | 17 | 20.0 |
| 8 | 19.0 | 18 | 20.5 |
| 9 | 20.5 | 19 | 19.0 |
| 10 | 21.5 | 20 | 21.5 |

As can be seen from these results, the reproducibility of quantitative analysis of arsenic is very good, and the analysis precision is also good.

Reference Example 2

The concentration of arsenic in petroleum fractions was analyzed as in Reference Example 1 using 100ml of various petroleum fractions containing organoarsenic compounds having various concentrations as shown in Table 4.

The results are shown in Table 4.

Reference Comparative Example 1

100ml of the same various petroleum fractions as those used in Reference Example 2 were burnt in an oxyhydrogen flame, and arsenic adhered to the wall surface of a combustion chamber was washed with hydrochloric acid. Thereafter, arsenic was absorbed into aqueous hydrogen peroxide. To this solution was then added magnesium nitrate and the mixture was evaporated to dryness. To this was added a 1% aqueous nitric acid solution. The resulting solution was introduced into an atomic absorption photometer to carry out the quantitative analysis of arsenic.

The results are shown in Table 4.

From one and one half day to two days were required for such a quantitative analysis of arsenic.

TABLE 4

| | Analysis Value obtained by Example 2 (ppb) | Analysis Value obtained by Comparative Example 1 (ppb) |
|-----------------|--|---|
| Light Naphtha-1 | 150 | 170 |
| Light Naphtha-2 | 51 | 47 |
| Heavy Naphtha-1 | 530 | 510 |
| Heavy Naphtha-2 | 10 | 9 |
| Kerosene | 170 | 190 |

According to the process for removing arsenic in the petroleum fraction of the present invention, arsenic in the petroleum fraction can be removed at a high percent removal by means of simple equipment. Even if highly reactive olefins are contained in the petroleum fraction, these olefins are not polymerized. Accordingly, arsenic in the petroleum fraction can be surely removed, and even if the arsenic-removed petroleum fraction is brought into contact with a catalyst, the catalyst is not poisoned.

Claims

1. A process for removing arsenic in a petroleum fraction which comprises the steps of contacting the petroleum fraction containing arsenic with an adsorbent, said adsorbent comprising a substrate having introduced thereinto a sulfur-containing component selected from mercapto moieties, thioethers, thioaldehydes, thiocarboxylic acids, dithiocarboxylic acid, thioamides and thiocyanates.

2. The process according to claim 1 wherein the substrate of the adsorbent is an active carbon, a bituminous coal, or an organic polymeric compound.

3. The process according to claim 2 wherein the organic polymeric compound as the substrate is polystyrene, styrene-divinylbenzene polymers, polyvinyl chloride, phenolic resins, cellulose or mixtures thereof.

4. The process according to any preceding claim wherein the sulfur-containing component is introduced in the form of a mercapto moiety.

Patentansprüche

1. Verfahren zur Entfernung von Arsen in einer Erdölfraction, das die Stufen des In-Kontakt-Bringens der Arsen enthaltenden Erdölfraction mit einem Adsorptionsmittel umfaßt, wobei das Adsorptionsmittel ein Substrat umfaßt, welches hierin eingebracht eine Schwefel enthaltende Komponente enthält, ausgewählt unter Mercapto-Anteilen, Thioethern, Thioaldehyden, Thiocarbonsäuren, Dithiocarbonsäuren; Thioamiden und Thiocyanaten.

2. Verfahren gemäß Anspruch 1, bei dem das Substrat des Adsorptionsmittels Aktivkohle, eine bituminöse Kohle bzw. Steinkohle oder eine organische polymere Verbindung ist.

3. Verfahren gemäß Anspruch 2, bei dem die als Substrat vorliegende organische polymere Verbindung Polystyrol, Styrol-Divinylbenzol-Polymere, Polyvinylchlorid, Phenolharze, Cellulose oder Mischungen hiervon ist.

4. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem die Schwefel enthaltende Verbindung in Form eines Mercapto-Anteils eingebracht ist.

Revendications

1. Procédé pour éliminer l'arsenic d'une fraction pétrolière, qui comprend les étapes de mise en contact de la fraction pétrolière contenant l'arsenic avec un adsorbant, ledit adsorbant comprenant un substrat dans lequel on a introduit un composant soufré choisi parmi des fragments mercapto, les thioéthers, les thioaldéhydes, les acides thiocarboxyliques, les acides dithiocarboxyliques, les thioamides et les thiocyanates.

2. Procédé selon la revendication 1, dans lequel le substrat est un charbon actif, un charbon bitumineux ou un composé organique polymère.

3. Procédé selon la revendication 2, dans lequel le composé organique polymère formant le substrat est constitué par du polystyrène, des polymères styrène-divinylbenzène, du poly(chlorure de vinyle), des résines phénoliques, de la cellulose ou des mélanges de ceux-ci.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel on introduit le composé soufré sous la forme d'un fragment mercapto.